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US-A- 2 819 958  
US-A- 4 067 734  
US-A- 4 299 626

NKK, "High Formability Titanium Alloy SP-700", Cat.No.300-158, March 1992

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## Description

The invention relates to the field of metallurgy and particularly to the field of titanium base alloys having excellent formability and method of making thereof and method of superplastic forming thereof.

5 Titanium alloys are widely used as aerospace materials, e.g., in aeroplanes and rockets since the alloys possess tough mechanical properties and are comparatively light.

However the titanium alloys are difficult material to work. When finished products have a complicated shape, the yield in terms of weight of the product relative to that of the original material is low, which causes a significant increase in the production cost.

10 In case of the most widely used titanium alloy, which is Ti-6Al-4V alloy, when the forming temperature becomes below 800 °C, the resistance to deformation increases significantly, which leads to the generation of defects such as cracks.

To avoid the disadvantage of high production cost, a new technology called superplastic forming which utilizes superplastic phenomena, has been proposed.

15 Superplasticity is the phenomenon in which materials under certain conditions, are elongated up to from several hundred to one thousand percent, in some case, over one thousand percent, without necking down.

One of the titanium alloys wherein the superplastic forming is performed is Ti-6Al-4V having the microstructure with the grain size of 5 to 10 micrometer.

20 However, even in case of the Ti-6Al-4V alloy, the temperature for superplastic forming ranges from 875 to 950 °C, which shortens the life of working tools or necessitates costly tools. U.S. Pat. No. 4,299,626 discloses titanium alloys in which Fe, Ni, and Co are added to Ti-6Al-4V to improve superplastic properties having large superplastic elongation and small deformation resistance.

25 However even with the alloy described in U.S. Pat. 4,229,626, which is Ti-6Al-4V-Fe-Ni-Co alloy developed to lower the temperature of the superplastic deformation of Ti-6Al-4V alloys, the temperature can be lowered by only 50 to 80 °C compared with that for Ti-6Al-4V alloy, and the elongation obtained at such a temperature range is not sufficient.

Moreover, this alloy contains 6 wt.% Al as in Ti-6Al-4V alloy, which causes the hot workability in rolling or forging, being deteriorated.

30 A titanium alloy is known from U.S. Patent 4,067,734 which shows improved resistance to stress corrosion cracking in comparison to proprietary Ti-6Al-4V alloy. This US Patented alloy has a nominal composition comprising 3.8 to 5.3 wt % Al; 2.5 to 4.25 wt % Mo; 2.5 to 4.25 wt % V; up to 4.0 wt % Zr; up to 1.25 wt % Fe; up to 2.2 wt % Cr; up to 1.0 wt % Ni, and balance Ti. The alloy is said to show improved combinations of strength and toughness which, in addition to its enhanced stress corrosion cracking resistance, make it attractive in aerospace applications. However, the high molybdenum content of this alloy renders it unsuitable for superplastic forming because the stress required to effect superplastic deformation is 35 unacceptably high.

40 In a technical article entitled "Complex Alloying of Titanium Alloys" by A I Khorev published in METALLOVEDENIE I TERMICHESKAYA OBRABOTKA METALLOV, No. 8, August 1975, pages 58-63 (English language translation available from METAL SCIENCE AND HEAT TREATMENT, Vol. 17, No. 8, pages 701-705), titanium alloys are disclosed in which constant concentrations of a single  $\alpha$ -stabiliser are used with differing amounts of isomorphous (Mo and V) and eutectoid-forming (Cr and Fe)  $\beta$ -stabilising elements. In all cases the  $\alpha$ -stabiliser is aluminium, which is present in fixed proportions of 3% by weight or 6% by weight. Khorev does not contemplate use of such alloys for superplastic forming and by virtue of the low aluminium content in the disclosed alloys having 3% by weight aluminium, strengths are low.

45 It is an object of the invention to provide a titanium alloy having improved superplastic properties.

More specifically, it is an object of the invention to provide a high strength titanium alloy with improved superplastic properties compared with the aforementioned Ti-6Al-4V, Ti-6Al-4V-Fe-Ni-Co and Ti-4Al-3Mo-3V-Fe-Cr-Ni-Zr alloys, having large superplastic elongation and small resistance of deformation in superplastic deformation and excellent hot workability in the production process, and good cold workability.

50 It is a further object of the invention to provide a method of making the above-mentioned titanium alloy.

It is another object of the invention to provide a method of superplastic forming of the above-mentioned titanium alloy.

According to a first aspect of the invention, there is provided a titanium base alloy comprising the following constituents in proportions by weight:

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aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

5

but excluding alloys having a molybdenum content of 2.5% by weight or higher, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

10

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\% \text{ and}$$

wherein

15

$$X\% = \% \text{Fe} + \% \text{Co} + (0.9 \times \% \text{Cr}), \text{ and}$$

$$Y\% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1.8 \times \% \text{Cr}) + (1.5 \times \% \text{V}) + \% \text{Mo}$$

and wherein the balance of the composition is titanium save for incidental impurities.

Preferably, the alloy has a grain size of alpha crystals of 5µm or less.

According to a second aspect of the invention there is provided a method of making a titanium base

20 alloy comprising the steps of:

(a) reheating the titanium base alloy specified below to a temperature in the temperature range from  $\beta$  transus minus 250 °C to  $\beta$  transus:

a titanium base alloy comprising the following constituents in proportions by weight:

25

aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

30

but excluding alloys having a molybdenum content of 2.5% by weight or higher, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

35

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\% \text{ and}$$

wherein

$$X\% = \% \text{Fe} + \% \text{Co} + (0.9 \times \% \text{Cr}), \text{ and}$$

40

$$Y\% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1.8 \times \% \text{Cr}) + (1.5 \times \% \text{V}) + \% \text{Mo}$$

and wherein the balance of the composition is titanium save for incidental impurities, and

(b) hot working the heated alloy with a reduction ratio of at least 50 %.

According to a third aspect of the invention, there is provided a method of superplastic forming a titanium base alloy comprising the steps of:

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(a) heat treating the titanium base alloy specified below to a temperature in the temperature range from  $\beta$  transus minus 250 °C to  $\beta$  transus:

a titanium base alloy comprising the following constituents in proportions by weight:

50

aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

55

but excluding alloys having a molybdenum content of 2.5% by weight or higher, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\% \text{ and}$$

wherein

5  $X\% = \% \text{Fe} + \% \text{Co} + (0.9 \times \% \text{Cr})$ , and

$Y\% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1.8 \times \% \text{Cr}) + (1.5 \times \% \text{V}) + \% \text{Mo}$

and wherein the balance of the composition is titanium save for incidental impurities, and

(b) superplastic forming the above heat-treated alloy.

10 These and other objects and features of the present invention will be apparent from the following detailed description.

Figure 1 shows the change of the maximum superplastic elongation of the titanium alloys with respect to the addition of Fe, Co, and Cr to Ti-Al-V-Mo alloy. The abscissa denotes Fe wt.% + Co wt.% + 0.9 X Cr wt.%, and the ordinate denotes the maximum superplastic elongation.

15 Figure 2 shows the change of the maximum superplastic elongation of the titanium alloys with respect to the addition of V, Mo, Fe, Co, and Cr to Ti-Al alloy.

The abscissa denotes  $2 \times \text{Fe wt.\%} + 2 \times \text{Co wt.\%} + (1.8 \times \text{Cr wt.\%}) + (1.5 \times \text{V wt.\%}) + \text{Mo wt.\%}$ , and the ordinate denotes the maximum superplastic elongation.

20 Figure 3 shows the change of the maximum superplastic elongation of the titanium alloys, having the same chemical composition with those of the invented alloys, with respect to the change of the grain size of  $\alpha$ -crystal thereof. The abscissa denotes the grain size of  $\alpha$ -crystal of the titanium alloys, and the ordinate denotes the maximum superplastic elongation.

Figure 4 shows the influence of Al content on the maximum cold reduction ratio without edge cracking.

Figure 5 shows the relationship between the hot reduction ratio and the maximum superplastic elongation.

25 The abscissa denotes the reduction ratio and the ordinate denotes the maximum superplastic elongation.

The bold curves denote those within the scope of the invention. The dotted curves denote those outside the scope of the invention.

The inventors find the following knowledge concerning the required properties.

- 30 (1) By adding a prescribed quantity of Al, the strength of titanium alloys can be enhanced.
- (2) By adding at least one element selected from the group of Fe, Co, and Cr to the alloy, and prescribing the value of Fe wt.% + Co wt.% + 0.9 X Cr wt.% in the alloy, the superplastic properties can be improved; the increase of the superplastic elongation and the decrease of the deformation resistance, and the strength thereof can be enhanced.
- 35 (3) By adding the prescribed quantity of Mo, the superplastic properties can be improved; the increase of the superplastic elongation and the lowering of the temperature wherein the superplasticity is realized, and the strength thereof can be enhanced.
- (4) By adding the prescribed quantity of V, the strength of the alloy can be enhanced.
- (5) By adding the prescribed quantity of O, the strength of the alloy can be enhanced.
- 40 (6) By prescribing the value of a parameter of beta stabilizer,  $2 \times \text{Fe wt.\%} + 2 \times \text{Co wt.\%} + (1.8 \times \text{Cr wt.\%}) + (1.5 \times \text{V wt.\%}) + \text{Mo wt.\%}$ , a sufficient superplastic elongation can be imparted to the alloy and the room temperature strength thereof can be enhanced.
- (7) By prescribing the grain size of the  $\alpha$ -crystal, the superplastic properties can be improved.
- (8) By prescribing the temperature and the reduction ratio in making the alloy, the superplastic properties can be improved.
- 45 (9) By prescribing the reheating temperature in heat treating of the alloy prior to the superplastic deformation thereof, the superplastic properties can be improved.

This invention is based on the above knowledge and briefly explained as follows.

50 The reason of the above specification concerning the chemical composition, the conditions of making and superplastic forming of the alloy is explained as below:

#### I. Chemical composition

##### (1) Al

55

Titanium alloys are produced ordinarily by hot-forging and/or hot rolling. However, when the temperature of the work is lowered, the deformation resistance is increased, and defects such as cracks are liable to generate, which causes the lowering of workability.

The workability has close relationship with Al content.

Al is added to titanium as  $\alpha$ -stabilizer for the  $\alpha + \beta$ -alloy, which contributes to the increase of mechanical strength. However in case that the Al content is below 3.42 wt.%, sufficient strength aimed in this invention can not be obtained, whereas in case that the Al content exceeds 5 wt.%, the hot deformation resistance is increased and cold workability is deteriorated, which leads to the lowering of the productivity.

Accordingly, Al content is determined to be 3.42 to 5.0% wt.%, and more preferably 4.0 to 5.0% wt.%.

#### (2) Fe, Co, and Cr

To obtain a titanium alloy having high strength and excellent superplastic properties, the micro-structure of the alloy should have fine equi-axed  $\alpha$  crystal, and the volume ratio of the  $\alpha$  crystal should range from 40 to 60%.

Therefore, at least one element from the group of Fe, Co, Cr, and Mo should be added to the alloy to lower the  $\beta$  transus compared with Ti-6Al-4V alloy.

As for Mo, explanation will be given later. Fe, Co, and Cr are added to titanium as  $\beta$ -stabilizer for the  $\alpha + \beta$ -alloy, and contribute to the enhancement of superplastic properties, that is, the increase of superplastic elongation, and the decrease of resistance of deformation, by lowering of  $\beta$ -transus, and to the increase of mechanical strength by constituting a solid solution in  $\beta$ -phase. By adding these elements the volume ratio of  $\beta$ -phase is increased, and the resistance of deformation is decreased in hot working the alloy, which leads to the evading of the generation of defects such as cracks. However this contribution is insufficient in case that the content of these elements is below 0.1 wt.%, whereas in case that the content exceeds 3.15 wt.%, these elements form brittle intermetallic compounds with titanium, and generate a segregation phase called "beta fleck" in melting and solidifying of the alloy, which leads to the deterioration of the mechanical properties, especially ductility.

Accordingly, the content of at least one element from the group of Fe, Co, Cr is determined to be from 0.1 to 3.15 wt.%.

As far as Fe content is concerned, a more preferred range is from 1.0 to 2.5 wt.%.

#### (3) $\text{Fe wt.\%} + \text{Co wt.\%} + 0.9 \times \text{Cr wt.\%}$

$\text{Fe wt.\%} + \text{Co wt.\%} + 0.9 \times \text{Cr wt.\%}$  is an index for the stability of  $\beta$ -phase which has a close relationship with the superplastic properties of titanium alloys, that is, the lowering of the temperature wherein superplasticity is realized and the deformation resistance in superplastic forming.

In case that this index is below 0.85 wt.%, the alloy loses the property of low temperature wherein the superplastic properties is realized which is the essence of this invention, or the resistance of deformation thereof in superplastic forming is increased when the above mentioned temperature is low.

In case that this index exceeds 3.15 wt.%, Fe, Co, and Cr form brittle intermetallic compounds with titanium, and generates a segregation phase called "beta fleck" in melting and solidifying of the alloy, which leads to the deterioration of the mechanical properties, especially ductility at room temperature. Accordingly, this index is determined to be 0.85 to 3.15 wt.%, and more preferably 1.5 to 2.5 wt.%.

#### (4) Mo

Mo is added to titanium as  $\beta$ -stabilizer for the  $\alpha + \beta$ -alloy, and contributes to the enhancement of superplastic properties, that is, the lowering of the temperature wherein the superplasticity is realized, by lowering of  $\beta$ -transus as in the case of Fe, Co, and Cr.

However this contribution is insufficient in case that Mo content is below 0.85 wt.%, whereas in case that Mo content exceeds 3.15 wt.% Mo increases the specific weight of the alloy due to the fact that Mo is a heavy metal, and the property of titanium alloys as high strength/weight material is lost. Moreover Mo has low diffusion rate in titanium, which increases the deformation stress. Accordingly, Mo content is determined as 0.85-3.15 wt.%, and a more preferable range is 1.5 to 3.15 wt.%.

#### (5) V

V is added to titanium as  $\beta$ -stabilizer for the  $\alpha + \beta$ -alloy, which contributes to the increase of mechanical strength without forming brittle intermetallic compounds with titanium. This is, V strengthens the alloy by making a solid solution with  $\beta$  phase. The fact wherein the V content is within the range of 2.1 to 3.7 wt.%, in this alloy, has the merit in which the scrap of the most solid Ti-6Al-4V can be utilized. However

in case that V content is below 2.1 wt.%, sufficient strength aimed in this invention can not be obtained, whereas in case that V content exceeds 3.7 wt.%, the superplastic elongation is decreased, by exceedingly lowering of the  $\beta$  transus.

Accordingly, V content is determined as 2.1-3.7 wt.%, and a more preferable range is 2.5 to 3.7 wt.%.  
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#### (6) O

O contributes to the increase of mechanical strength by constituting a solid solution mainly in  $\alpha$ -phase. However in case that O content is below 0.01 wt.%, the contribution is not sufficient, whereas in case that the O content exceeds 0.15 wt.%, the ductility at room temperature is deteriorated. Accordingly, the O content is determined to be 0.01 to 0.15 wt.%, and a more preferable range is 0.06 to 0.14.  
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(7)  $2 \times \text{Fe wt.}\% + 2 \times \text{Co wt.}\% + (1.8 \times \text{Cr wt.}\%) + (1.5 \times \text{V wt.}\%) + \text{Mo wt.}\%$

$2 \times \text{Fe wt.}\% + 2 \times \text{Co wt.}\% + 1.8 \times \text{Cr wt.}\% + (1.5 \times \text{V wt.}\%) + \text{Mo wt.}\%$  is an index showing the stability of  $\beta$ -phase, wherein the higher the index the lower the  $\beta$  transus and vice versa. The most pertinent temperature for the superplastic forming is the value at which the volume ratio of primary  $\alpha$ -phase is from 40 to 60 percent. The temperature has close relationship with the  $\beta$ -transus. When the index is below 7 wt.%, the temperature wherein the superplastic properties are realized, is elevated, which diminishes the advantage of the invented alloys as low temperature and the contribution thereof to the enhancement of the room temperature strength. When the index exceeds 13 wt.%, the temperature wherein the volume ratio of primary  $\alpha$ -phase is from 40 to 60 percent becomes too low, which causes the insufficient diffusion and hence insufficient superplastic elongation. Accordingly,  $2 \times \text{Fe wt.}\% + 2 \times \text{Co wt.}\% + (1.8 \times \text{Cr wt.}\%) + (1.5 \times \text{V wt.}\%) + \text{Mo wt.}\%$  is determined to be 7 to 13 wt.%, and a more preferable range is 9 to 11 wt.%.  
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#### II. The grain size of $\alpha$ -crystal

When superplastic properties are required, the grain size of the  $\alpha$ -crystal is preferred to be below 5  $\mu$  m.

The grain size of  $\alpha$ -crystal has close relationship with the superplastic properties, the smaller the grain size the better the superplastic properties. In this invention, in case that the grain size of  $\alpha$ -crystal exceeds 5  $\mu$  m, the superplastic elongation is decreased and the resistance of deformation is increased. The superplastic forming is carried out by using comparatively small working force, e.g. by using low gas pressure. Hence smaller resistance of deformation is required.  
30

Accordingly, the grain size of  $\alpha$ -crystal is determined as below 5  $\mu$  m, and a more preferable range is below 3  $\mu$  m.  
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#### III. The conditions of making the titanium alloy

##### (1) The conditions of hot working

The titanium alloy having the chemical composition specified in I is formed by hot forging, hot rolling, or hot extrusion, after the cast structure of the alloy is broken down by forging or slabbing and the structure is made uniform. At this stage of the hot working, in case that the reheating temperature of the work is below  $\beta$  transus minus 250 °C, the deformation resistance becomes excessively large or defects such as cracks may be generated. When the temperature exceeds  $\beta$ -transus, the grain of the crystal becomes coarse which causes deterioration of the hot workability such as generation of cracks at the grain boundary.  
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When the reduction ratio is below 50% sufficient strain is not accumulated in the  $\alpha$ -crystal, and the fine equi-axed micro-structure is not obtained, whereas the  $\alpha$ -crystal stays elongated or coarse. These structures are not only unfavourable to superplastic deformation, but also inferior in hot workability and cold workability. Accordingly, the reheating temperature at the stage of working is from  $\beta$ -transus minus 250 °C to  $\beta$ -transus, and the reduction ratio is at least 50%, and more preferably at least 70%.  
50

##### (2) Heat treatment

This process is required for obtaining the equi-axed fine grain structure in the superplastic forming of the alloy. When the temperature of the heat treatment is below  $\beta$ -transus minus 250 °C, the recrystallization is not sufficient, and equi-axed grain cannot be obtained. When the temperature exceeds  $\beta$ -transus,  
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th micro-structure becomes  $\beta$ -phase, and equi-axed  $\alpha$ -crystal vanishes, and superplastic properties are not obtain d. Accordingly the heat tr atm nt temperature is required to b from  $\beta$ -transus minus 250 °C to  $\beta$ -transus.

This heat treatment can be done b for th sup rplastic forming in the forming apparatus.

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#### Examples

##### Example 1

10 Tables 1, 2, and 3 show the chemical composition, the grain size of  $\alpha$ -crystal, the mechanical properties at room temperature, namely, 0.2% proof stress, tensile strength, and elongation, the maximum cold reduction ratio without edge cracking, and the superplastic properties, namely, the maximum superplastic elongation, the temperature wherein the maximum superplastic deformation is realised, the maximum stress of deformation at said temperature and the resistance of deformation in hot compression at 700 °C, of  
15 invented titanium alloys; A1 to A28, of conventional Ti-6Al-4V alloys; B1 to B4, of titanium alloys for comparison; C1 to C20. These alloys are molten and worked in the following way.

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Table 1(1)

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	Test Nos.	Chemical Composition (wt.%) (Balance Ti)						
		Al	V	Mo	O	Fe	Co	Cr
Alloys of Present Invention	A1	4.65	3.30	1.68	0.11	2.14	-	-
	A3	4.03	2.11	0.88	0.09	3.11	-	-
	A4	4.93	2.17	2.37	0.03	0.91	-	-
	A6	3.97	2.97	2.02	0.08	1.91	-	-
	A7	3.67	2.54	0.97	0.05	2.81	-	-
	A8	4.16	3.50	1.65	0.04	2.90	-	-
	A9	3.42	3.26	1.76	0.07	2.53	-	-
	A11	3.97	3.14	1.86	0.12	-	1.94	-
	A12	4.03	3.27	2.29	0.06	-	-	0.99
	A13	4.37	3.11	2.15	0.10	-	-	1.87
	A14	4.02	2.76	2.07	0.08	-	-	2.24
	A15	4.03	2.85	2.21	0.07	-	-	2.75
	A16	3.54	3.17	2.27	0.07	0.86	-	1.56
	A17	4.23	3.43	2.31	0.08	1.66	-	0.96
	A18	3.97	2.67	1.86	0.07	1.21	-	1.06
	A20	4.36	3.11	2.04	0.11	1.74	0.74	-
	A21	4.21	2.56	2.27	0.06	-	0.97	2.32
	A25	4.40	2.96	1.83	0.09	1.21	0.41	0.67
	A27	4.61	3.97	2.11	0.08	1.07	-	-
	A28	4.32	2.99	1.07	0.09	1.06	-	-

Table 1 (1) (Continued from the previous page)

Test Nos.	Chemical Composition (wt.%) (Balance Ti)		Grain Size of $\alpha$ -Crystal ( $\mu\text{m}$ )
	Fe+Co+0.9xCr	2Fe+2Co+1.8Cr+1.5V+Mo	
A1	2.14	10.9	2.3
A3	3.11	10.3	3.7
A4	0.91	7.1	2.8
A6	1.91	10.3	2.1
A7	2.81	10.4	4.6
A8	2.90	12.7	2.8
A9	2.53	11.7	3.0
A11	1.94	10.5	4.0
A12	0.89	9.0	4.2
A13	1.68	10.2	3.3
A14	2.02	10.2	3.0
A15	2.48	9.0	3.8
A16	2.26	11.6	3.2
A17	2.52	12.5	2.2
A18	2.16	10.2	3.5
A20	2.48	11.7	2.5
A21	3.06	12.2	2.9
A25	2.22	10.7	3.9
A27	1.07	10.2	6.8
A28	1.06	7.7	9.0

Alloys of  
Present  
Invention

Table 1(2)

	Test Nos.	Chemical Composition (wt.%) (Balance Ti)							
		Al	V	Mo	O	Fe	Ni	Co	Cr
Prior Art Alloys	B1	6.03	4.25	-	0.17	0.25	-	-	-
	B2	6.11	4.07	-	0.12	0.08	-	-	-
	B3	6.17	4.01	-	0.19	1.22	-	0.91	-
	B4	6.24	3.93	-	0.19	0.22	0.93	0.88	-
	C1	2.96	3.01	0.87	0.06	0.91	-	-	-
	C2	5.27	3.17	1.78	0.12	1.69	-	-	-
	C3	4.21	2.78	0.82	0.07	1.03	-	-	-
	C4	3.17	2.21	3.21	0.08	2.99	-	-	-
	C5	3.06	2.99	1.18	0.09	0.81	-	-	-
	C6	3.66	2.11	3.00	0.11	3.27	-	-	-
	C7	3.21	2.01	2.25	0.06	0.87	-	-	-
	C8	4.67	3.82	1.79	0.07	2.44	-	-	-
	C9	4.57	3.91	1.34	0.16	1.78	-	-	-
	C10	3.07	2.11	2.75	0.11	0.92	-	-	-
	C11	4.87	2.69	0.86	0.07	0.90	-	-	-
	C12	3.21	4.05	2.40	0.10	2.46	-	-	-
	C13	4.17	3.08	1.21	0.08	-	-	-	0.65
	C14	3.76	2.14	2.76	0.10	-	-	-	3.85
	C15	3.86	2.76	1.96	0.13	0.13	-	-	0.42
	C16	4.10	2.11	0.96	0.11	-	3.43	-	-
	C17	3.95	2.24	1.07	0.08	-	-	3.52	-
	C18	4.08	3.06	1.79	0.07	2.14	-	-	1.52
	C19	4.13	2.61	1.43	0.13	0.11	0.14	0.13	0.11
	C20	3.87	3.31	2.04	0.08	1.76	0.86	0.72	0.31
	C21	3.92	3.69	3.02	0.12	0.96	-	-	-
	C22	3.07	2.82	1.17	0.13	1.79	-	-	-

Table 1(2) (Continued from the previous page)

	Test Nos.	Chemical Composition (wt.%) (Balance Ti)		Grain Size of a-Crystal (um)
Prior Art Alloys	B1	0.25	6.9	6.2
	B2	0.08	6.3	6.7
	B3	2.13	6.0	3.5
	B4	2.03	10.0	4.1
Alloys for Comparison	C1	0.91	7.2	5.3
	C2	1.69	9.9	3.2
	C3	1.03	7.1	6.2
	C4	2.99	12.5	3.9
	C5	0.81	7.3	4.8
	C6	3.27	12.7	2.7
	C7	0.87	7.0	3.7
	C8	2.44	12.4	4.6
	C9	1.78	10.8	5.0
	C10	0.92	7.8	5.6
	C11	0.90	6.7	4.6
	C12	2.46	13.4	3.7
	C13	0.59	7.0	4.9
	C14	3.47	12.9	3.2
	C15	0.51	7.1	4.4
	C16	3.43	11.0	6.0
	C17	3.52	11.5	5.5
	C18	3.51	13.4	4.8
	C19	0.48	6.3	5.8
	C20	3.62	14.2	3.0
	C21	0.96	10.5	1.9
	C22	1.79	9.0	3.3

Table 2

	Test Nos.	Tensile Properties at Room Temperature		
		0.2% PS	TS	EL
		(kgf/mm <sup>2</sup> )		(%)
Alloys of Present Invention	A1	94.5	98.0	20.0
	A3	90.3	93.6	21.8
	A4	95.1	99.0	17.8
	A6	93.6	96.8	20.7
	A7	94.7	97.9	19.6
	A8	96.7	100.4	17.2
	A9	95.0	98.3	17.8
	A11	94.3	97.3	18.9
	A12	90.3	94.1	21.7
	A13	94.1	97.6	20.6
	A14	92.3	94.9	21.1
	A15	93.6	96.2	20.5
	A16	95.1	98.5	17.1
	A17	96.7	100.5	17.2
	A18	92.8	96.2	21.3
	A20	95.1	98.7	17.2
	A21	95.4	99.0	17.0
	A25	93.9	97.5	21.0
	A27	98.2	104.0	13.7
	A28	94.6	99.6	19.4

Table 2 (Continued from the previous page)

	Test Nos.	Tensile Properties at Room Temperature		
		0.2% PS	TS	EL
		(kgf/mm <sup>2</sup> )		(%)
Prior Art Alloys	B1	85.9	93.3	18.9
	B2	82.7	90.1	20.2
	B3	104.2	108.5	17.4
	B4	102.5	106.8	21.0
Alloys for Comparison	C1	85.3	89.7	22.0
	C2	98.7	105.7	12.7
	C3	83.7	88.6	20.5
	C4	101.9	107.6	11.7
	C5	86.1	89.9	20.6
	C6	100.6	110.4	13.2
	C7	93.7	97.4	20.1
	C8	96.4	103.4	16.7
	C9	99.6	106.3	16.1
	C10	90.5	94.7	21.4
	C11	85.6	90.7	19.0
	C12	103.6	107.9	14.2
	C13	92.7	96.4	17.1
	C14	102.1	104.7	18.7
	C15	90.4	93.7	21.1
	C16	103.1	104.9	4.6
	C17	102.9	105.0	5.1
	C18	103.7	106.1	8.3
	C19	90.7	93.3	21.1
	C20	103.6	105.7	6.0
	C21	93.1	96.3	20.9
	C22	88.7	92.0	21.9

Table 3 (1)

	Test Nos.	Cold Reduction Ratio without Edge Cracking (%)	Maximum Super- plastic Elongation (%)	Tempera- ture, at which Maximum Elongation is Shown (°C)	Deformation Stress at Temperature at which Maximum Elongation is Shown (kgf/mm <sup>2</sup> )	Deformation Stress in Hot Compression Test (kgf/mm <sup>2</sup> )
Alloys of Present Invention	A1	55	2040	775	1.45	24
	A3	60	1680	775	1.38	21
	A4	50	1970	800	1.08	24
	A6	60	1860	775	1.44	23
	A7	65	1710	775	1.47	21
	A8	55	1690	775	1.26	24
	A9	65	1855	750	1.58	22
	A11	60	1800	775	1.32	21
	A12	70 or more	1610	800	1.30	22
	A13	50	1720	775	1.43	24
	A14	60	2010	775	1.39	22
	A15	55	2000	775	1.37	22
	A16	65	1850	775	1.28	21
	A17	50	1900	750	1.25	24
	A18	60	2050	800	1.10	23
	A20	50	1810	775	1.22	24
	A21	55	1630	750	1.47	23
	A25	55	1890	775	1.32	24
	A27	50	1310	775	1.62	24
	A28	55	970	775	1.69	24



Table 3 (2)

	Test Nos.	Cold Reduction Ratio without Edge Cracking (%)	Maximum Super-plastic Elongation (%)	Temperature, at which Maximum Elongation is Shown (°C)	Deformation Stress at Temperature at which Maximum Elongation (kgf/mm <sup>2</sup> )	Deformation Stress in Hot Compression Test (kgf/mm <sup>2</sup> )
Prior Art Alloys	B1	10 or less	982	875	1.25	37
	B2	10 or less	925	900	1.03	35
	B3	10 or less	1328	825	1.07	30
	B4	10 or less	1385	825	1.02	31
Alloys for Comparison	C1	70 or more	-	-	-	-
	C2	30	-	-	-	29
	C3	50	-	-	-	25
	C4	45	750	750	2.27	27
	C5	70 or more	-	-	-	-
	C6	40	700	750	2.31	28
	C7	60	1220	775	1.45	26
	C8	20	-	-	-	-
	C9	10 or less	-	-	-	-
	C10	60	1320	775	1.52	25
	C11	30	1625	850	1.07	28
	C12	70 or less	1225	750	2.01	27
	C13	60	1250	850	1.00	28
	C14	10 or less	-	-	-	-
	C15	55	1500	850	1.08	28
	C16	30	-	-	-	-
	C17	30	-	-	-	-
	C18	40	1050	750	2.22	27
	C19	50	1250	850	1.12	29
	C20	20	-	-	-	-
	C21	65	2250	750	1.61	22
	C22	70 or more	1750	775	1.39	20

The ingots are molten in an arc furnace under argon atmosphere, which are hot forged and hot rolled into plates with thickness of 50mm. At the working stage, the reheating temperature is of the  $\alpha + \beta$  dual phase and the reduction ratio is 50 to 80%. After the reduction, the samples are treated by a recrystallization annealing in the temperature range of the  $\alpha + \beta$  dual phase.

The samples from these plates are tested concerning their mechanical properties at room temperature, namely, 0.2% proof stress, tensile strength, and elongation, as shown in Table 2.

As for the tensile test for superplasticity, samples are cut out of the plates with dimensions of the parallel part; 5mm width by 5mm length by 4mm thickness and tested under atmospheric pressure of  $5.0 \times 10^{-6}$  Torr. The test results are shown in Table 3, denoting the maximum superplastic elongation, the temperature wherein the maximum superplastic elongation is realized, the maximum deformation stress at said temperature, and the deformation resistance in hot compression at 700 °C of the samples shown in Table 1. The maximum deformation stress is obtained by dividing the maximum test load by original sectional area.

The test results of resistance of deformation in hot compression are shown in Table 3. In this test cylindrical specimens are cut out from the hot rolled plate. The specimens are hot compressed at 700 °C under vacuum atmosphere. The test results are evaluated by the value of true stress when the samples are compressed with the reduction ratio of 50%. The invented alloys have the value of below 24 kgf/mm<sup>2</sup> which is superior to those of the conventional alloy, Ti-4V-6Al and the alloys for comparison.

This hot compression test was not carried out for the alloys for comparison C1, C3, and C5 since the values of the tensile test at room temperature are below 90 kgf/mm<sup>2</sup> which is lower than those of Ti-6Al-4V, and not for the alloys for comparison, C2, C8, C9, C14, C16, C17, and C20 since the maximum cold reduction ratio without edge cracking is below 30% which is not in the practical range.

Figures 1 to 5 are the graphs of the test results.

Figure 1 shows the change of the maximum superplastic elongation of the titanium alloys with respect to the addition of Fe, Co, and Cr to Ti-Al-V-Mo alloy.

The abscissa denotes Fe wt.% + Co wt.% + 0.9 x Cr wt.%, and the ordinate denotes the maximum superplastic elongation. As is shown in Figure 1, the maximum superplastic elongation of over 1500 % is obtained in the range of 0.85 to 3.15 wt.% of the value of Fe wt.% + Co wt.% + 0.9 x Cr wt.%, and higher values are observed in the range of 1.5 to 2.5 wt.%.

Figure 2 shows the change of the maximum superplastic elongation of the titanium alloys with respect to the addition of V, Mo, Fe, Co, and Cr to Ti-Al alloy. The abscissa denotes  $2 \times \text{Fe wt.\%} + 2 \times \text{Co wt.\%} + (1.8 \times \text{Cr wt.\%}) + (1.5 \times \text{V wt.\%}) + \text{Mo wt.\%}$ , and the ordinate denotes the maximum superplastic elongation. As shown in Figure 2, the maximum superplastic elongation of over 1500% is obtained in the range of 7 to 13 wt.% of the value of  $2 \times \text{Fe wt.\%} + 2 \times \text{Co wt.\%} + (1.8 \times \text{Cr wt.\%}) + (1.5 \times \text{V wt.\%}) + \text{Mo wt.\%}$ , and higher values are observed in the range of 9 to 11 wt.%. When the index is below 7 wt.%, the temperature wherein the maximum superplastic elongation is realized, is 850 °C.

Figure 3 shows the change of the maximum superplastic elongation of the titanium alloys, having the same chemical composition with those of the invented alloys, with respect to the change of the grain size of  $\alpha$ -crystal thereof. The abscissa denotes the grain size of  $\alpha$ -crystal of the titanium alloys, and the ordinate denotes the maximum superplastic elongation.

As shown in the Figure 3, large elongations of over 1500% are obtained in case that the grain size of  $\alpha$ -crystal is 5  $\mu$  m or less, and higher values are observed below the size of 3  $\mu$  m.

Figure 4 shows the influence of Al content on the maximum cold reduction ratio without edge cracking. The abscissa denotes Al wt.%, and the ordinate denotes the maximum cold reduction ratio without edge cracking.

As shown in the Figure 4, the cold rolling with the cold reduction ratio of more than 50% is possible when the Al content is below 5 wt.%.

As shown in Tables 2 and 3, the tensile properties of the invented alloys A1 to A28 are 92 kgf/mm<sup>2</sup> or more in tensile strength, 13% or more in elongation, and the alloys possess the tensile strength and the ductility equal to or superior to Ti-6Al-4V alloys. The invented alloys can be cold rolled with the reduction ratio of more than 50%.

Furthermore, in case of the invented alloys A1 to 26 having the grain size of the crystal of below 5  $\mu$  m, the temperature wherein the maximum superplastic elongation is realized is as low as 800 °C, and the maximum superplastic elongation at the temperature is over 1500%, whereas in case of the alloys for comparison, the superplastic elongation is around 1000% or less, or 1500% in C 15, however, the temperature for the realization of superplasticity in C15 is 850 °C.

Accordingly, the invented alloys are superior to the alloys for comparison in superplastic properties.

In case of the alloys for comparison C1, C3, and C5, the superplastic tensile test is not carried out since the result of the room temperature tensile test thereof is 90 kgf/mm<sup>2</sup> which is inferior to that of Ti-6Al-4V alloy.

In case of the alloys for comparison C2, C8, C9, C14, C16, C17, and C20, the superplastic tensile test is not carried out since the maximum cold reduction ratio without edge cracking thereof is below 30%, and

out of the practical range.

### Example 2

- For the titanium alloys D1 and D2 with the chemical composition shown in Table 4, the hot working and heat treatment are carried out according to the conditions specified in Table 5, and the samples are tested as for the superplastic tensile properties, cold reduction test, and hot workability test.

Table 4

	Chemical Composition (wt.%) (Balance Ti)						
	Al	V	Mo	O	Fe	Co	Cr
D1	4.65	3.30	1.68	0.11	2.14	-	-
D2	4.02	2.76	2.07	0.08	-	-	2.24
	Chemical Composition (wt.%) (Balance Ti)						
	Fe + Co + 0.9 Cr			2Fe + 2Co + 1.8Cr + 1.5V + Mo			
D1	2.14			10.9			
D2	2.02			10.2			

Table 5

		$\beta$ -Transus (°C)	Final Hot Working			Temperature of Heat Treatment (°C)	Maximum Super- plastic Elongation (%)	Hot Workability Test
			Heating Temp. (°C)	Reduction Ratio	Crack			
D1	1	915	600	4	Crack	-	-	-
	2		800	4	No Crack	775	2040	No Crack
	3		1100	4	Crack	-	-	-
	4		800	1.5	No Crack	775	1450	Crack
	5		800	4	No Crack	1000	500	Crack
D2	1	910	650	4	Crack	-	-	-
	2		850	4	No Crack	775	2010	No Crack
	3		850	4	No Crack	950	600	No Crack

- The method of the test as for the superplastic properties and the cold reduction without edge cracking is the same with that shown in Example 1. The hot workability test is carried out with cylindrical specimens having the dimensions; 6mm in diameter, 10mm in height with a notch parallel to the axis of the cylinder having the depth of 0.8mm, at the temperature of about 700 °C, compressed with the reduction of 50%. The criterion of this test is the generation of crack.

- The heat treatment and the superplastic tensile test and the other tests are not carried out as for the samples D1-1, D1-3, and D2-1, since cracks are generated on these samples after the hot working.

Figure 5 shows the relationship between the hot reduction ratio and the maximum superplastic elongation.

The abscissa denotes the reduction ratio and the ordinate denotes the maximum superplastic elongation.

In this figure the samples are reheated to the temperature between the  $\beta$ -transus minus 250 °C and  $\beta$ -transus. The samples having the reduction ratio of at least 50% possess the maximum superplastic elongation of over 1500%, and in case of the ratio of at least 70%, the elongation is over 1700%. The results are also shown in Table 5.

As shown in Table 5, as for the samples of which reheating temperature is within the range from  $\beta$ -transus minus 250 °C to  $\beta$ -transus and of which reduction ratio exceeds 50%, heat treatment condition being from  $\beta$ -transus minus 200 °C to  $\beta$ -transus in reheating temperature, the value of the maximum superplastic elongation exceeds 1500%, and the maximum cold reduction ratio without edge cracking is at least 50%. As for the samples of which conditions are out of the above specified range, the value of the maximum superplastic elongation is below 1500%, and cracks are generated on the notched cylindrical specimens for evaluating the hot workability, or the maximum cold reduction ratio without edge cracking is below 50%.

### Example 3

Table 7 shows the results of the deformation resistance of hot compression of the invented and conventional alloys with the chemical composition specified in Table 6.

Table 6

(wt.%) (balance Ti)

	Al	V	Mo	O	Fe	Cr	
E1	4.65	3.30	1.68	0.11	2.14	-	Alloys of the Present Invention
E2	3.97	2.67	1.68	0.07	1.21	1.06	
E3	6.11	4.07	-	0.12	0.08	-	Conventional Alloy

Table 7

	Tempe- rature	600 °C		800 °C	
	Strain Rate	$10^{-3}(S^{-1})$	$1(S^{-1})$	$10^{-3}(S^{-1})$	$1(S^{-1})$
E1	Deformation Stress (kgf/ mm <sup>2</sup> )	20.0	38.8	3.2	15.0
E2		19.5	36.9	3.0	14.6
E3		32.1	62.1	7.6	22.0

The samples with the dimensions; 8mm in diameter and 12 mm in height, are tested by applying compressive force thereon under vacuum atmosphere, and the true strain true stress curves are obtained.

The values shown in Table 7 are the stress  $\sigma$  at the strain of 50%.

The stress values of the invented alloy are smaller than those of the conventional alloy by 30 to 50%, both at higher strain rate,  $1 s^{-1}$  and at low strain rate,  $10^{-3} s^{-1}$ , and both at 600 °C and 800 °C, which proves the invented alloy having the superior workability not only in superplastic forming but in iso-thermal

forging and ordinary hot forging.

# Claims

- 5 1. A titanium base alloy comprising the following constituents in proportions by weight:

aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

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- 15 but excluding alloys in which the molybdenum content is 2.5% by weight or greater, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\%$$

20

wherein

$$X\% = \%Fe + \%Co + (0.9 \times \%Cr)$$

and

$$Y\% = (2 \times \%Fe) + (2 \times \%Co) + (1.8 \times \%Cr) + (1.5 \times \%V) + \%Mo$$

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and wherein the balance of the composition is titanium save for incidental impurities.

2. A titanium base alloy as claimed in claim 1, further characterised in that the aluminium content is 4 to 5 % by weight.
3. A titanium base alloy as claimed in claim 1 or claim 2, further characterised in that the vanadium content is 2.5 to 3.7 % by weight.
4. A titanium base alloy as claimed in any preceding claim, further characterised in that the molybdenum content is 1.5 to 2.37 % by weight.
- 35 5. A titanium base alloy as claimed in any preceding claim, further characterised in that the value of X% is defined as follows:

$$1.5\% \leq X\% \leq 2.5\%.$$

40

6. A titanium base alloy as claimed in any preceding claim, further characterised in that the value of Y% is defined as follows:

$$9\% \leq Y\% \leq 11\%.$$

45

7. A titanium base alloy as claimed in claim 1, further characterised in that the group of optional elements consists of iron and cobalt.
- 50 8. A titanium base alloy as claimed in claim 1, further characterised in that the group of optional elements consists of iron and chromium.
9. A titanium base alloy as claimed in claim 1, further characterised in that the optional element is iron.
- 55 10. A titanium base alloy as claimed in claim 9, further characterised in that the iron content is 1.0 to 2.5 % by weight.

11. A titanium base alloy as claimed in claim 10, further characterised in that the iron content is 1.5 to 2.5 % by weight.

12. A titanium base alloy as claimed in any one of claims 7 to 11, further characterised in that the aluminium content is 4.0 to 5.0 % by weight, the vanadium content is 2.5 to 3.7 % by weight and the molybdenum content is 1.5 to 2.37 % by weight.

13. A titanium base alloy as claimed in claim 12, further characterised in that the value of Y% is defined as follows:

$$9 \% \leq Y\% \leq 11 \%$$

14. A titanium base alloy as claimed in any preceding claim, further characterised in that the grain size of the alpha crystals is less than 5  $\mu\text{m}$ .

15. A method of making a titanium base alloy comprising the steps of :

(a) reheating the titanium base alloy specified below to a temperature in the range from 250 °C below the  $\beta$ -transus temperature of the alloy composition to its  $\beta$ -transus temperature, the specified alloy composition comprising the following constituents in proportions by weight:

aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

but excluding alloys in which the molybdenum content is 2.5% by weight or greater, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\%$$

wherein

$$X\% = \%Fe + \%Co + (0.9 \times \%Cr)$$

and

$$Y\% = (2 \times \%Fe) + (2 \times \%Co) + (1.8 \times \%Cr) + (1.5 \times \%V) + \%Mo$$

wherein the balance of the composition is titanium save for incidental impurities, and

(b) hot working the heated alloy with a reduction ratio of at least 50%.

16. A method as claimed in claim 15, further characterised in that the reduction ratio is at least 70%.

17. A method as claimed in claims 15 or 16, further characterised in that the values for X% and Y% are defined as follows:

$$0.85 \% \leq X\% \leq 1.5 \%$$

$$7 \% \leq Y\% \leq 9 \%$$

18. A method as claimed in claims 15 or 16, further characterised in that the values for X% and Y% are defined as follows:

$$1.5 \% \leq X\% \leq 2.5 \%$$

$$9 \% \leq Y\% \leq 11 \%$$

19. A method as claimed in claims 15 or 16, further characterised in that the values for X% and Y% are defined as follows:

$$2.5 \% \leq X\% \leq 3.15 \%$$

$$11 \% \leq Y\% \leq 13 \%$$

20. A method as claimed in any one of claims 15 to 18, further characterised in that the aluminium content is defined as follows:

$$4.0 \text{ wt.}\% \leq \text{Al} \leq 5.0 \text{ wt.}\%$$

21. A method of superplastic forming a titanium base alloy comprising the steps of :

(a) heat treating a titanium base alloy composition as specified below to a temperature within the range from 250 °C below the  $\beta$ -transus temperature of the alloy composition to its  $\beta$ -transus temperature, the specified alloy composition comprising the following constituents in proportions by weight:

aluminium	3.42 - 5.0 %
vanadium	2.1 - 3.7 %
molybdenum	0.85 - 3.15 %
oxygen	0.01 - 0.15 %

but excluding alloys in which the molybdenum content is 2.5% by weight or greater, and further comprising at least one of the elements selected from the group consisting of iron, cobalt and chromium in proportions by weight satisfying the following equations:

$$0.85\% \leq X\% \leq 3.15\%$$

$$7\% \leq Y\% \leq 13\%$$

wherein

$$X\% = \% \text{Fe} + \% \text{Co} + (0.9 \times \% \text{Cr})$$

and

$$Y\% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1.8 \times \% \text{Cr}) + (1.5 \times \% \text{V}) + \% \text{Mo}$$

wherein the balance of the composition is titanium save for incidental impurities, and

(b) superplastic forming the heat treated alloy composition.

22. A method as claimed in claim 21 further characterised in that the values for X% and Y% are defined as follows:

$$0.85 \% \leq X\% \leq 1.5 \%$$

$$7 \% \leq Y\% \leq 9 \%$$

23. A method as claimed in claim 21 further characterised in that the values for X% and Y% are defined as follows:

$$1.5 \% \leq X\% \leq 2.5 \%$$

$$9 \% \leq Y\% \leq 11 \%$$

24. A method as claimed in claim 21 further characterised in that the values for X% and Y% are defined as follows:

$$2.5 \% \leq X\% \leq 3.15 \%$$

$$11 \% \leq Y\% \leq 13 \%$$



## Patentansprüche

1. Legierung auf Titanbasis, umfassend die folgenden Bestandteile in Gewichtsanteilen:

Aluminium	3,42 - 5,0 %
Vanadium	2,1 - 3,7 %
Molybdän	0,85 - 3,15 %
Sauerstoff	0,01 - 0,15 %

unter Ausschluß von Legierungen, bei denen der Molybdängehalt 2,5 Gew.-% oder größer ist, und umfassend weiterhin wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus Eisen, Kobalt und Chrom in Gewichtsanteilen, entsprechend den folgenden Gleichungen:

$$0,85 \% \leq X \% \leq 3,15 \%$$

$$7 \% \leq Y \% \leq 13 \%$$

worin

$$X \% = \% \text{ Fe} + \% \text{ Co} + (0,9 \times \% \text{ Cr})$$

und

$$Y \% = (2 \times \% \text{ Fe}) + (2 \times \% \text{ Co}) + (1,8 \times \% \text{ Cr}) + (1,5 \times \% \text{ V}) + \% \text{ Mo}$$

und worin der Rest der Zusammensetzung Titan und zufallsbedingte Verunreinigungen sind.

2. Legierung auf Titanbasis gemäß Anspruch 1, weiterhin gekennzeichnet **dadurch**, daß der Aluminiumgehalt 4 bis 5 Gew.-% beträgt.
3. Legierung auf Titanbasis gemäß Anspruch 1 oder Anspruch 2, weiterhin gekennzeichnet **dadurch**, daß der Vanadengehalt 2,5 bis 3,7 Gew.-% beträgt.
4. Legierung auf Titanbasis gemäß Anspruch einem der vorhergehenden Ansprüche, weiterhin gekennzeichnet **dadurch**, daß der Molybdängehalt 1,5 bis 2,37 Gew.-% beträgt.
5. Legierung auf Titanbasis gemäß einem der vorhergehenden Ansprüche, weiterhin gekennzeichnet **dadurch**, daß der Wert für X % wie folgt definiert ist:

$$1,5 \% \leq X \% \leq 2,5 \%$$

6. Legierung auf Titanbasis gemäß einem der vorhergehenden Ansprüche, weiterhin gekennzeichnet **dadurch**, daß der Wert für Y % wie folgt definiert ist:

$$9 \% \leq Y \% \leq 11 \%$$

7. Legierung auf Titanbasis gemäß Anspruch 1, weiterhin gekennzeichnet **dadurch**, daß die Gruppe der gegebenenfalls verwendeten Elemente aus Eisen und Kobalt besteht.
8. Legierung auf Titanbasis gemäß Anspruch 1, weiterhin gekennzeichnet **dadurch**, daß die Gruppe der gegebenenfalls verwendeten Elemente aus Eisen und Chrom besteht.
9. Legierung auf Titanbasis gemäß Anspruch 1, weiterhin gekennzeichnet **dadurch**, daß das gegebenenfalls verwendete Element Eisen ist.
10. Legierung auf Titanbasis gemäß Anspruch 9, weiterhin gekennzeichnet **dadurch**, daß der Eisengehalt 1,0 bis 2,5 Gew.-% beträgt.

11. Legierung auf Titanbasis gemäß Anspruch 10, weiterhin gekennzeichnet **dadurch**, daß der Eisengehalt 1,5 bis 2,5 Gew.-% beträgt.

12. Legierung auf Titanbasis gemäß einem der Ansprüche 7 bis 11, weiterhin gekennzeichnet **dadurch**, daß der Aluminiumgehalt 4,0 bis 5 Gew.-% ist, der Vanadiumgehalt 2,5 bis 3,7 Gew.-% ist, und der Molybdängehalt 1,5 bis 2,37 Gew.-% ist.

13. Legierung auf Titanbasis gemäß Anspruch 12, weiterhin gekennzeichnet **dadurch**, daß der Wert von Y % wie folgt definiert ist:

$$9 \% \leq Y \% \leq 11 \%$$

14. Legierung auf Titanbasis gemäß einem der vorhergehenden Ansprüche, weiterhin gekennzeichnet **dadurch**, daß die Korngröße der alpha-Kristalle weniger als 5 µm ist.

15. Verfahren zur Herstellung einer Legierung auf Titanbasis umfassend die Stufen:

(a) Wiedererhitzen der Legierung auf Titanbasis gemäß der nachfolgenden Spezifizierung auf eine Temperatur in dem Bereich von 250 °C unterhalb der  $\beta$ -Übergangstemperatur der Legierungszusammensetzung bis zu deren  $\beta$ -Übergangstemperatur, wobei die angegebene Legierungszusammensetzung die folgenden Bestandteile in Gewichtsanteilen umfaßt:

Aluminium	3,42 - 5,0 %
Vanadium	2,1 - 3,7 %
Molybdän	0,85 - 3,15 %
Sauerstoff	0,01 - 0,15 %

unter Ausschluß von Legierungen, bei denen der Molybdängehalt 2,5 Gew.-% oder größer ist, und weiterhin umfassend wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus Eisen, Kobalt und Chrom, in Gewichtsanteilen, entsprechend den nachfolgenden Gleichungen

$$0,85 \% \leq X \% \leq 3,15 \%$$

$$7 \% \leq Y \% \leq 13 \%$$

worin

$$X \% = \% \text{ Fe} + \% \text{ Co} + (0,9 \times \% \text{ Cr})$$

und

$$Y \% = (2 \times \% \text{ Fe}) + (2 \times \% \text{ Co}) + (1,8 \times \% \text{ Cr}) + (1,5 \times \% \text{ V}) + \% \text{ Mo},$$

worin der Rest der Zusammensetzung Titan und zufallsbedingte Verunreinigungen sind, und (b) Warmverarbeitung der erwärmten Legierung mit einem Reduktionsverhältnis von wenigstens 50 %.

16. Verfahren gemäß Anspruch 15, weiterhin gekennzeichnet **dadurch**, daß das Reduktionsverhältnis wenigstens 70 % ist.

17. Verfahren gemäß Ansprüchen 15 oder 16, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$0,85 \% \leq X \% \leq 1,5 \%$$

$$7 \% \leq Y \% \leq 9 \%$$

18. Verfahren gemäß Ansprüchen 15 oder 16, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$1,5 \% \leq X \% \leq 2,5 \%$$

$$9 \% \leq Y \% \leq 11 \%$$

19. Verfahren gemäß Ansprüchen 15 oder 16, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$2,5 \% \leq X \% \leq 3,15 \%$$

$$11 \% \leq Y \% \leq 13 \%$$

20. Verfahren gemäß einem der Ansprüche 15 bis 18, weiterhin gekennzeichnet **dadurch**, daß der Aluminiumgehalt wie folgt definiert ist:

$$4,0 \text{ Gew.}\% \leq \text{Al} \leq 5,0 \text{ Gew.}\%$$

21. Verfahren zur superplastischen Formgebung einer Legierung auf Titanbasis, umfassend die Stufen  
(a) Wärmebehandeln einer Legierungszusammensetzung auf Titanbasis der nachfolgenden Spezifizierung auf eine Temperatur in einem Bereich von 250 °C unterhalb der  $\beta$ -Übergangstemperatur der Legierungszusammensetzung bis zu deren  $\beta$ -Übergangstemperatur, wobei die angegebene Legierungszusammensetzung die folgenden Bestandteile in Gewichtsanteilen enthält:

Aluminium	3,42 - 5,0 %
Vanadium	2,1 - 3,7 %
Molybdän	0,85 - 3,15 %
Sauerstoff	0,01 - 0,15 %

unter Ausschluß von Legierungen, bei denen der Molybdängehalt 2,5 Gew.-% oder größer ist, und umfassend weiterhin wenigstens ein Element, ausgewählt aus der Gruppe bestehend aus Eisen, Kobalt und Chrom in Gewichtsanteilen, entsprechend den folgenden Gleichungen:

$$0,85 \% \leq X \% \leq 3,15 \%$$

$$7 \% \leq Y \% \leq 13 \%$$

worin

$$X \% = \% \text{Fe} + \% \text{Co} + (0,9 \times \% \text{Cr})$$

und

$$Y \% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1,8 \times \% \text{Cr}) + (1,5 \times \% \text{V}) + \% \text{Mo},$$

worin der Rest der Zusammensetzung Titan und zufallsbedingte Verunreinigungen sind, und

(b) superplastische Formgebung der wärmebehandelten Legierungszusammensetzung.

22. Verfahren gemäß Anspruch 21, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$0,85 \% \leq X \% \leq 1,5 \%$$

$$7 \% \leq Y \% \leq 9 \%$$

23. Verfahren gemäß Anspruch 21, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$1,5 \% \leq X \% \leq 2,5 \%$$

$$9 \% \leq Y \% \leq 11 \%$$

24. Verfahren gemäß Anspruch 21, weiterhin gekennzeichnet **dadurch**, daß die Werte für X % und Y % wie folgt definiert sind: , daß die Werte für X % und Y % wie folgt definiert sind:

$$2,5 \% \leq X \% \leq 3,15 \%$$

$$11 \% \leq Y \% \leq 13 \%$$

## Revendications

1. Un alliage à base de titane comprenant les constituants suivants en proportions en poids :

aluminium	3,42 - 5,0 %
vanadium	2,1 - 3,7 %
molybdène	0,85 - 3,15 %
oxygène	0,01 - 0,15 %

mais à l'exclusion des alliages ayant une teneur en molybdène de 2,5% en poids ou plus élevée, et comportant en outre au moins un des éléments choisis dans le groupe constitué du fer, du cobalt, et du chrome en proportions pondérales satisfaisant aux équations suivantes :

$$0,85 \% \leq X \% \leq 3,15 \%$$

$$7 \% \leq Y \% \leq 13 \% \text{ et}$$

dans lesquelles

$$X \% = \% \text{ Fe} + \% \text{ Co} + (0,9 \times \% \text{ Cr}), \text{ et}$$

$$Y \% = (2x\% \text{ Fe}) + (2x\% \text{ Co}) + (1,8x\% \text{ Cr}) + (1,5x\% \text{ V}) + \% \text{ Mo}$$

et dans lesquelles le reste de la composition est constitué par du titane à l'exception des impuretés éventuelles.

2. Un alliage à base de titane tel que revendiqué dans la revendication 1, caractérisé en outre en ce que la teneur en alumine est de 4 à 5 % poids.
3. Un alliage à base de titane tel que revendiqué dans la revendication 1 ou la revendication 2, caractérisé en outre en ce que la teneur en vanadium est de 2,5 à 3,7 % poids.
4. Un alliage à base de titane tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en outre en ce que la teneur en molybdène est de 1,5 à 2,37 % poids.
5. Un alliage à base de titane tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en outre en ce que la valeur de X % est définie de la manière suivante :

$$1,5 \% \leq X \% \leq 2,5 \%$$

6. Un alliage à base de titane tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en outre en ce que la valeur de Y % est définie de la manière suivante :

$$9 \% \leq Y \% \leq 11 \%$$

7. Un alliage à base de titane tel que revendiqué dans la revendication 1, caractérisé en outre en ce que le groupe d'éléments facultatifs est constitué du fer et du cobalt.
8. Un alliage à base de titane tel que revendiqué dans la revendication 1, caractérisé en outre en ce que d'éléments facultatifs est constitué du fer et du chrome.
9. Un alliage à base de titane tel que revendiqué dans la revendication 1, caractérisé en ce que l'élément facultatif est le fer.
10. Un alliage à base de titane tel que revendiqué dans la revendication 9, caractérisé en outre en ce que la teneur en fer est de 1,0 à 2,5 % en poids.

11. Un alliage à base de titane tel que revendiqué dans la revendication 10, caractérisé en outre en ce que la teneur en fer est de 1,5 à 2,5 % en poids.

12. Un alliage à base de titane tel que revendiqué dans l'une quelconque des revendications 7 à 11, caractérisé en outre en ce que la teneur en aluminium est de 4,0 à 5,0 % en poids, la teneur en vanadium est de 2,5 à 3,7 % en poids et la teneur en molybdène est de 1,5 à 2,37 % en poids.

13. Un alliage à base de titane tel que revendiqué dans la revendication 12, caractérisé en outre en ce que la valeur de Y % est définie de la manière suivante :

$$9 \% \leq Y \% \leq 11 \%$$

14. Un alliage à base de titane tel que revendiqué dans l'une des revendications précédentes, caractérisé en outre en ce que la dimension des grains des cristaux- $\alpha$  est inférieure à 5  $\mu\text{m}$ .

15. Un procédé pour fabriquer un alliage à base de titane comportant les étapes de :

(a) réchauffer l'alliage à base de titane spécifié ci-dessous à une température dans la gamme de température du point de transition- $\beta$  moins 250 °C jusqu'au point de transition- $\beta$ : un alliage à base de titane comportant les constituants suivants en proportion pondérale :

aluminium	3,42 - 5,0 %
vanadium	2,1 - 3,7 %
molybdène	0,85 - 3,15 %
oxygène	0,01 - 0,15 %

mais à l'exclusion des alliages ayant un teneur en molybdène de 2,5 % poids ou plus élevé et comportant en outre au moins des éléments choisis dans le groupe constitué du fer, du cobalt, et du chrome en proportions pondérales qui satisfont aux équations :

$$\begin{aligned} 0,85 \% \leq X \% \leq 3,15 \% \\ 7 \% \leq Y \% \leq 13 \% \text{ et} \end{aligned}$$

dans laquelle

$X \% = \% \text{Fe} + \% \text{Co} + (0,9 \times \% \text{Cr})$  et,  
 $Y \% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1,8 \times \% \text{Cr}) + (1,5 \times \% \text{V}) + \% \text{Mo}$   
 et dans lequel le reste de la composition est du titane à l'exception des impuretés éventuelles et,  
 (b) façonner à chaud l'alliage chauffé avec un taux de réduction de 50 %.

16. Un procédé tel que revendiqué dans la revendication 15, caractérisé en outre en ce que le rapport de réduction est d'au moins 70 %.

17. Un procédé tel que revendiqué dans la revendication 15 ou 16, caractérisé en outre en ce que les valeurs pour X % et Y % sont définies de la manière suivante :

$$\begin{aligned} 0,85 \% \leq X \% \leq 1,5 \% \\ 7 \% \leq Y \% \leq 9 \% \end{aligned}$$

18. Un procédé tel que revendiqué dans les revendications 15 ou 16, caractérisé en outre en ce que les valeurs X % et Y % sont définies de la manière suivante :

$$\begin{aligned} 1,5 \% \leq X \% \leq 2,5 \% \\ 9 \% \leq Y \% \leq 11 \% \end{aligned}$$

19. Un procédé tel que revendiqué dans les revendications 15 ou 16, caractérisé en outre en ce que les valeurs pour X % et Y % sont définies de la manière suivante :

$$2,5 \% \leq X \% \leq 3,15 \%$$

$$11 \% \leq Y \% \leq 13 \%$$

20. Un procédé tel que revendiqué dans une quelconque des revendications 15 à 18, caractérisé en outre en ce que la teneur en aluminium est définie de la manière suivante :

$$4,0 \% \text{ en poids } \leq \text{Al} \leq 5,0 \% \text{ en poids}$$

21. Un procédé de formage superplastique d'un alliage à base de titane comportant les étapes de:  
 (a) traiter par chauffage une composition d'alliage à base de titane comme spécifié ci-dessous à une température dans la gamme de 250 °C en dessous de la température du point de transition- $\beta$  de la composition alliée jusqu'à sa température de transition- $\beta$ , la composition d'alliage spécifiée comportant les constituants suivants en proportions pondérales :

aluminium	3,42 - 5,0 %
vanadium	2,1 - 3,7 %
molybdène	0,85 - 3,15 %
oxygène	0,01 - 0,15 %

mais à l'exclusion des alliages ayant une teneur en molybdène de 2,5% poids ou plus élevée et comportant en outre au moins un des éléments choisis dans le groupe constitué du fer, du cobalt, et du chrome en proportions pondérales qui satisfont aux équations :

$$0,85 \% \leq X \% \leq 3,15 \%$$

$$7 \% \leq Y \% \leq 13 \% \text{ et}$$

dans laquelle

$$X \% = \% \text{Fe} + \% \text{Co} + (0,9 \times \% \text{Cr}), \text{ et}$$

$$Y \% = (2 \times \% \text{Fe}) + (2 \times \% \text{Co}) + (1,8 \times \% \text{Cr}) + (1,5 \times \% \text{V}) + \% \text{Mo}$$

et dans lequel le reste de la composition est du titane à l'exception des impuretés éventuelles et  
 (b) réaliser le formage superplastique de l'alliage traité thermiquement.

22. Un procédé tel que revendiqué dans la revendication 21, caractérisé en outre en ce que les valeurs X % et Y % sont définies de la manière suivante :

$$0,85 \% \leq X \% \leq 1,5 \%$$

$$7 \% \leq Y \% \leq 9 \%$$

23. Un procédé tel que revendiqué dans la revendication 21, caractérisé en outre en ce que les valeurs pour X % et Y % sont définies de la manière suivante :

$$1, \% \leq X \% \leq 2,5 \%$$

$$9 \% \leq Y \% \leq 13 \%$$

24. Un procédé tel que revendiqué dans la revendication 21, caractérisé en outre en ce que les valeurs pour X % et Y % sont définies de la manière suivante :

$$2,5 \% \leq X \% \leq 3,15 \%$$

$$11 \% \leq Y \% \leq 13 \%$$

FIG. 1

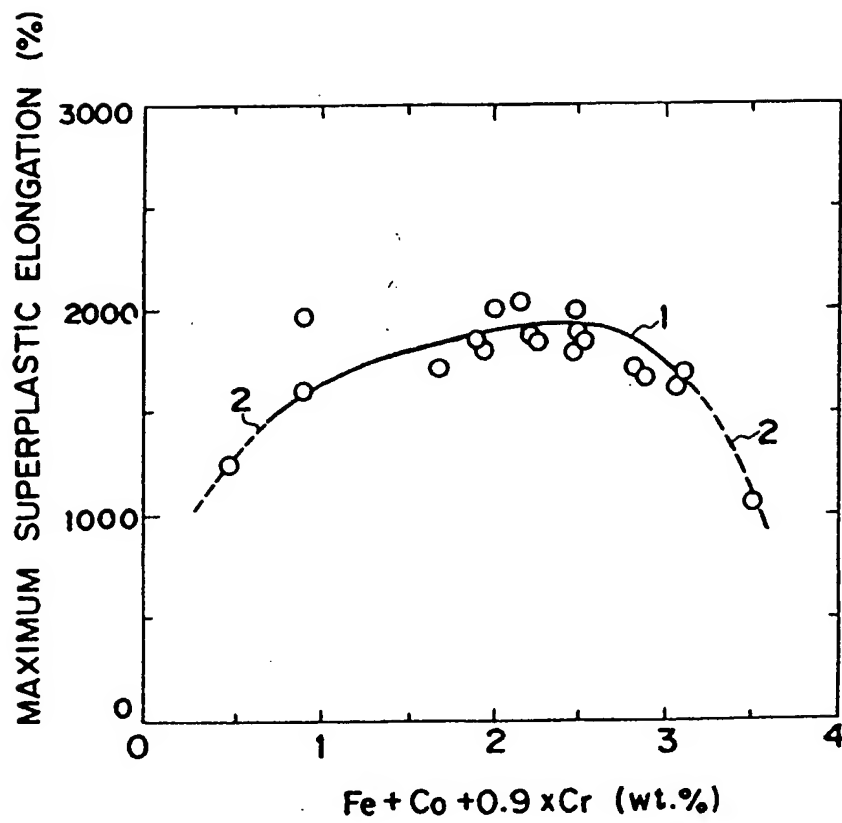


FIG. 2

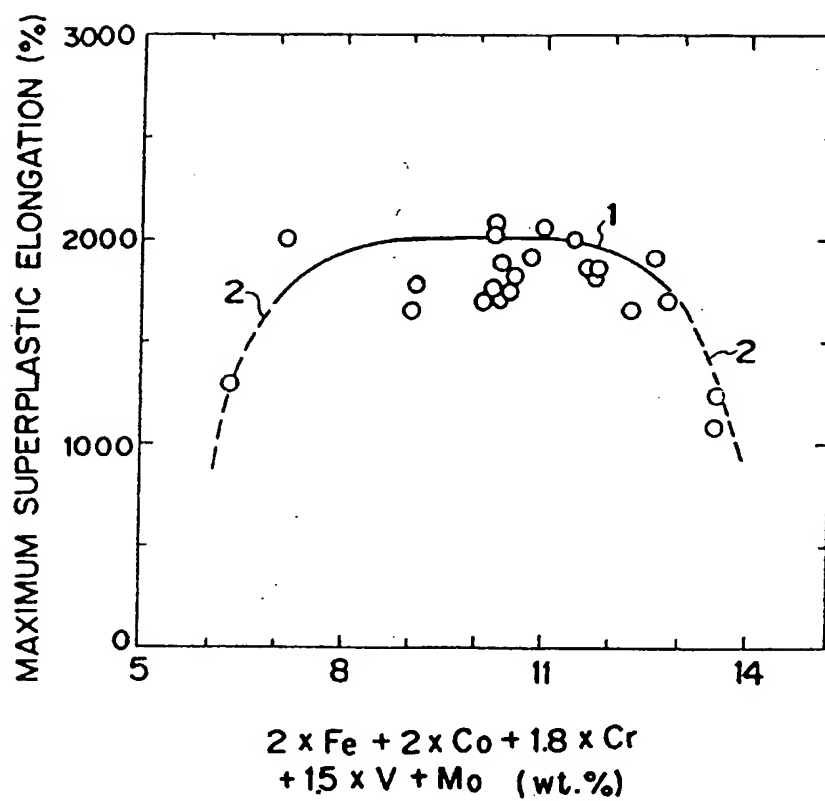




FIG. 3

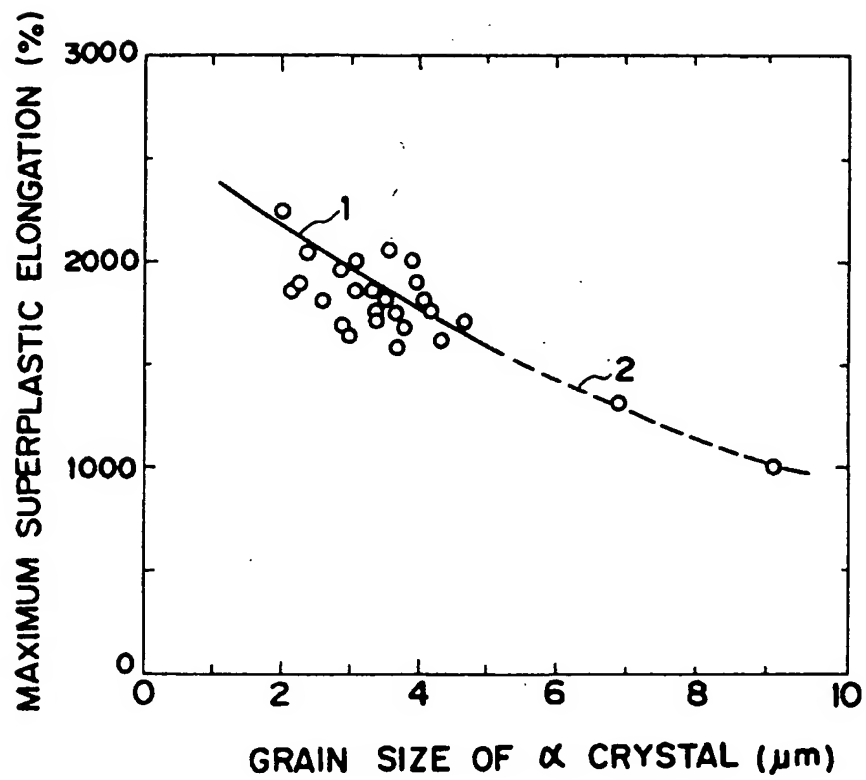


FIG. 4

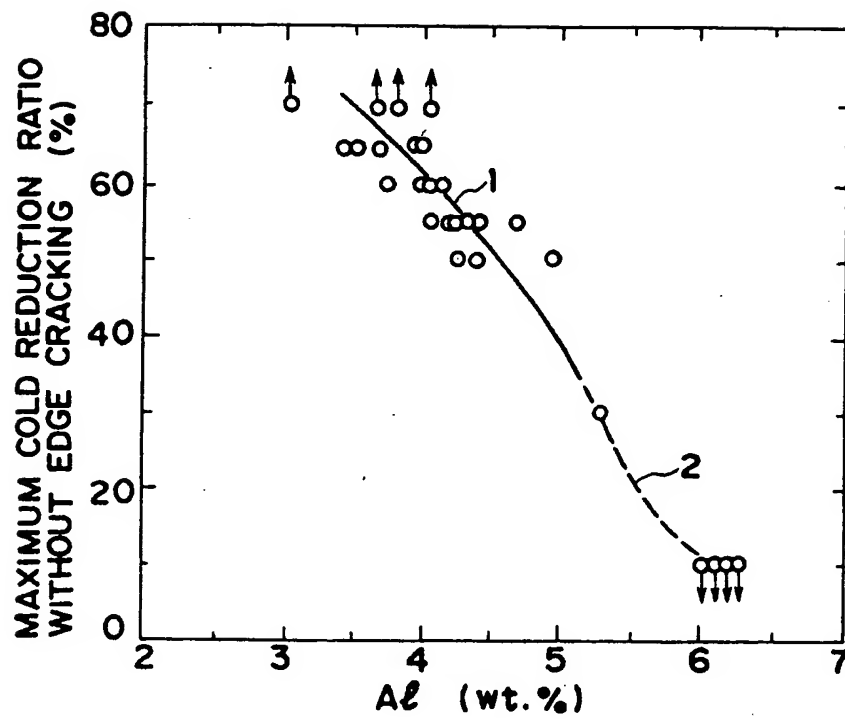


FIG. 5

